

JOINT INVENTORS


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## **APPLICATION FOR UNITED STATES LETTERS PATENT SPECIFICATION**

TO ALL WHOM IT MAY CONCERN:

Be it known that we, Osamu SEKIGUCHI, a citizen of Japan, c/o  
Nihon Hyomen Kagaku Kabushiki Kaisha, Chigasaki Factory, 1136, Hagisono,  
Chigasaki-shi, Kanagawa-ken Japan, and Shigetaka USUI, a citizen of Japan, c/o  
Nihon Hyomen Kagaku Kabushiki Kaisha, Chigasaki Factory, 1136, Hagisono,  
Chigasaki-shi, Kanagawa-ken Japan, have invented a new and useful METHOD FOR  
SUPPLYING ZINC IONS TO ALKALINE ZINC PLATING SOLUTION, of which the  
following is a specification.

## SPECIFICATION

### TITLE OF THE INVENTION

Method for supplying zinc ions to alkaline zinc plating solution

### BACKGROUND OF THE INVENTION

【0001】

### FIELD OF THE INVENTION

The present invention relates to a method for supplying zinc ions to an alkaline zinc plating solution.

【0002】

### PROIR ART

In zinc electro-plating of general materials, a non-cyanide alkaline zincate bath (hereinafter called "zincate bath") has been widely used since it has advantages in corrosion resistance, throwing power, environmental effect and the like. However, in the zincate bath, since metal zinc used for an anode is nonuniformly passivated, fluctuation of cathode current density distribution increases, and thickness of plated film, gloss, properties of film and the like are adversely affected. Moreover, since insoluble substances such as oxide (called "anode slime") formed by passivation of zinc pollute a plating solution, passivation of zinc anode is a cause of degradation of plating quality. Therefore, there arises an extreme opinion that the quality of zinc plating depends on the control of anode.

【0003】

To avoid the adverse effect of zinc anode on the plating solution, methods for supplying zinc ions from other than a plating anode, in which an insoluble anode is used, are suggested. For example, Japanese patent No.58-6792B discloses a method in which zinc dissolution is

accelerated by forming a cell between zinc and metal which generates higher hydrogen overvoltage than zinc in another dissolution tank. However, this method was disadvantageous in that a large dissolution bath was required since zinc dissolution rate was low and that a quantitative control of zinc dissolution was difficult since deactivation of zinc surface proceeded and zinc dissolution rate became extremely low as time elapsed. Additionally, Japanese patent No.57-149498A discloses an electrolytic method using zinc as an anode. However, this method was disadvantageous in that enough zinc dissolution rate could not be achieved and the same power as that for zinc plating was additionally required since passivation of anode zinc occurred when anode current was increased in order to accelerate the zinc dissolution rate.

#### 【 0 0 0 4 】

[Patent literature 1]

Japanese patent No. 58-6792B

[Patent literature 2]

Japanese patent No. 57-149498A

#### 【 0 0 0 5 】

### SUMMARY OF THE INVENTION

Accordingly, one object of the invention is to make the rate of zinc ions supply faster than that of zinc ions consumption, and to stabilize and control the zinc dissolution rate in order to stably maintain and control zinc ion concentration in an alkaline zinc plating solution.

#### 【 0 0 0 6 】

After having extensively conducted researches to solve the problems, the inventors have reached a method for supplying zinc ions to an alkaline zinc plating bath, wherein a source of zinc ions and a zinc dissolution accelerating metal are brought into electrically direct or

indirect contact with each other, and the source of zinc ions and the zinc dissolution accelerating metal are shaken, vibrated or rotated in a plating solution in order to accelerate zinc dissolution from the source of zinc ions.

More specifically, the inventors have reached the method for supplying zinc ions to the alkaline zinc plating bath, wherein the source of zinc ions and the zinc dissolution accelerating metal are put in the same vessel and brought into direct contact with each other, or put in different vessels and connected via an electric conductor, and the source of zinc ions and the zinc dissolution accelerating metal are moved in the vessel or vessels in the plating solution by shaking, vibrating or rotating the vessel or vessels in order to accelerate zinc dissolution.

Furthermore, the inventors have found out that the zinc dissolution rate could become several times higher than ever and stabilize at a high level by carrying out the above-mentioned method for supplying zinc ions to the alkaline zinc plating bath, by using one or more kinds selected from zinc, zinc alloy, zinc or zinc alloy whose surface is plated or contacted with metal that is more electropositive than zinc as the source of zinc ions, and by using; 1) metal that is more electropositive than zinc, 2) metal that is more electropositive than zinc, with which one or more kinds selected from iron, cobalt, nickel, carbon, silicon, manganese, chromium, molybdenum and tungsten are contacted, 3) metal that is more electropositive than zinc, in which one or more kinds selected from iron, cobalt, nickel, carbon, silicon, manganese, chromium, molybdenum and tungsten are dispersed, 4) alloy comprising metal that is more electropositive than zinc and one or more kinds selected from iron, cobalt, nickel, carbon, silicon, manganese, chromium, molybdenum and tungsten, or 5) composite or mixture of two or

more kinds selected from above 1) to 4) as the zinc dissolution accelerating metal.

#### 【0007】

#### DESCRIPTION OF THE SPECIAL EMBODIMENTS

The method of the present invention for supplying zinc ions can be applied to alkaline zincate bath zinc plating, alkaline cyanide bath zinc plating, alkaline zinc alloy plating such as zinc-iron, zinc-cobalt, zinc-nickel and zinc-manganese, and alkaline zinc composite plating such as zinc-silica and zinc-resin. The zincate bath zinc plating is the most effective among them.

#### 【0008】

The invention provides a method for supplying zinc ions to an alkaline zinc plating solution by means of zinc dissolution, which utilizes a difference in hydrogen overvoltage between the source of zinc ions and the zinc dissolution accelerating metal. The inventors have found out zinc dissolution accelerating metals that can much improve the zinc dissolution rate and that the zinc dissolution rate is much increased by a method wherein the source of zinc ions and the zinc dissolution accelerating metal are put in a vessel or vessels and moved in a plating solution by shaking, vibrating or rotating, etc., which causes agitation and mutual friction, to activate their surfaces. Moreover, the invention has achieved to provide a stably high dissolution rate and an easy control of zinc ion concentration in the plating solution.

#### 【0009】

As the source of zinc ions in the invention, metal zinc can be used. In order to make the dissolution rate faster, zinc alloy comprising zinc and metal that is more electropositive than zinc such as iron, nickel, cobalt, copper, silver, platinum and gold, or zinc to whose surface metal that is more electropositive than zinc such as iron, nickel,

cobalt, copper, silver, platinum and gold is deposited by plating, substituting or the like methods can be used.

#### 【 0 0 1 0 】

As the zinc dissolution accelerating metal in the invention, 1) metal that is more electropositive than zinc, 2) metal that is more electropositive than zinc, with which one or more kinds selected from iron, cobalt, nickel, carbon, silicon, manganese, chromium, molybdenum and tungsten are contacted, 3) metal that is more electropositive than zinc, in which one or more kinds selected from iron, cobalt, nickel, carbon, silicon, manganese, chromium, molybdenum and tungsten are dispersed, 4) alloy comprising metal that is more electropositive than zinc and one or more kinds selected from iron, cobalt, nickel, carbon, silicon, manganese, chromium, molybdenum and tungsten, or 5) a composite or mixture of two or more kinds selected from above 1) to 4) can be used. It is noted that oxides of iron, chromium, molybdenum and tungsten can be also used in case of above 3) or 4).

#### 【 0 0 1 1 】

The followings are the concrete examples of the zinc dissolution accelerating metal. Almost all kinds of metal that is more electropositive than zinc can be used but iron, nickel, cobalt and the like are advantageous from an economical point of view. Carbon alloyed metal, carbon dispersed metal or metal contacted with carbon, such as carbon impregnated metal (alloy), carburizing steel to whose surface carbon is adhered after dissolving its surface by an acid or the like (combination of alloy and contact), iron casting such as gray iron casting and malleable iron casting (combination of alloy and dispersion), carbon dispersed copper plating, carbon dispersed nickel plating and carbon dispersed cobalt plating onto metal that is more electropositive than zinc (combination of dispersion and contact), iron

plating, nickel plating, cobalt plating, copper plating, silver plating, platinum plating, gold plating and the like onto the surface of carbon (contact), can be also used. And as metal that includes one or more kinds among chromium, molybdenum and iron, metal that is more electropositive than zinc to which chromium oxide, molybdenum oxide or iron oxide is adhered (contact), dispersed iron plating, dispersed copper plating, dispersed nickel plating and dispersed cobalt plating on metal that is more electropositive than zinc wherein chromium oxide, molybdenum oxide, iron oxide or the like is dispersed in the plating (combination of dispersion and contact) and chromium molybdenum steel (alloy), etc, can be mentioned.

#### 【 0 0 1 2 】

The source of zinc ions and the zinc dissolution accelerating metal are put in the same vessel and brought into direct contact with each other or put in different vessels and connected via an electric conductor, and the vessel or vessels are shaken, vibrated or rotated, etc. in a plating solution to move the source of zinc ions and the zinc dissolution accelerating metal, which causes agitation of solution and mutual friction of metal surfaces and accelerates the zinc dissolution. Moreover, the friction maintains an activated state of the surface of the source of zinc ions and the zinc dissolution accelerating metal and keeps the dissolution rate high.

#### 【 0 0 1 3 】

Shapes and materials of the vessels used in the invention are not particularly restricted, provided that the vessels can receive the source of zinc ions and the zinc dissolution accelerating metal. Iron or iron castings which are the zinc dissolution accelerating metal of the invention can be also used as materials for the vessels such as baskets or barrels, for instance.

Sizes and shapes of the source of zinc ions and the zinc dissolution accelerating metal are not particularly restricted. But it is preferred to make their surface areas larger in order to increase the amount of zinc dissolution and make operations such as shaking, vibrating and rotating easier.

The ratio of the surface area of the source of zinc ions to that of the zinc dissolution accelerating metal can not strictly be specified since the surface area of the source of zinc ions constantly varies due to zinc dissolution and cannot be determined.

#### 【0014】

Thus, zinc dissolution to the plating solution is accelerated and the rate of zinc dissolution becomes faster than that of zinc ions consumption by the plating operation. And then, controlling the degree of contact both or either of the source of zinc ions and the zinc dissolution accelerating metal have with the plating solution in response to the analysis of zinc ion concentration in the plating solution enables automatic control of zinc ion concentration in the alkaline zinc plating bath, which contributes to quality stabilization of zinc plating products.

#### 【0015】

##### Examples

The followings describe examples of supplying zinc ions to the alkaline zinc plating solution by means of zinc dissolution, wherein vessels are rotated, which is a representative method of the invention, and comparative examples, wherein vessels are not rotated.

The dissolution test was implemented according to the following procedure. The test system was prepared in such a manner that the plating solution was overflowed from a plating bath (3 Litter) to a dissolution bath (2 Litter) and recycled to the plating bath through a



filter. In the plating bath, a temperature adjusting apparatus and a barrel plating apparatus were provided. In the dissolution bath, a plastic rotatable mini-barrel apparatus (5 rpm) was provided (examples 1 to 10 and comparative examples 1 to 12), and a plastic plating mini-barrel containing the source of zinc and a plastic plating mini-barrel containing the zinc dissolution accelerating metal were provided and the contents in the both barrels were connected via the electric conductor (examples 11 to 14 and comparative examples 13 to 16).

As the plating solution, the following zinc plating zincate bath, zinc plating cyanide bath, alkaline zinc-iron alloy plating bath and alkaline zinc-nickel alloy plating bath were used. The following source of zinc ions and the following zinc dissolution accelerating metal were put into the rotatable mini-barrels in the dissolution bath in such ratio that the total surface area of the source of zinc ions is almost equal to that of the zinc dissolution accelerating metal and zinc dissolution was implemented. The barrel or barrels were pulled out of the plating solution in the dissolution bath to stop zinc dissolution temporarily when zinc ion concentration in the plating solution increased by 2 g/L. Subsequently, zinc ion concentration in the plating solution was decreased by 2 g/L by means of electrodeposition of zinc before the barrels were again immersed in the plating solution and zinc ion concentration was increased by 2 g/L. This procedure was repeated 5 times. Time required to increase zinc ion concentration by 2 g/L at the first time and the fifth time were respectively compared with the comparative examples.

Zinc ion concentration was measured every 30 minutes. In case where zinc ion concentration did not increase by 2 g/L after 480 min of operation, the test was stopped and regarded as "no increase".

**【0016】**

The followings are the sources of zinc ions, the zinc dissolution accelerating metals and the plating solutions used in the example.

The source of zinc ions;

- A. Zinc grains (diameter 3 to 8 mm)
- B. Iron-substituted zinc grains (diameter 3 to 8 mm)
- C. Nickel-substituted zinc grains (diameter 3 to 8 mm)

The zinc dissolution accelerating metal;

- (1) Iron grains (diameter about 8 mm)
- (2) Cobalt plating iron grains (diameter about 8 mm)
- (3) Carbon dispersed cobalt plating iron grains (diameter about 8 mm)
- (4) Iron casting grains (diameter 15 to 30 mm, gray cast iron)
- (5) Chromium molybdenum steel chips (about 5 mm square)
- (6) None

The plating solution;

1. Zinc plating zincate bath

zinc ions	10 g/L
sodium hydroxide	120 g/L

2. Zinc plating cyanide bath

zinc ions	20 g/L
sodium hydroxide	60 g/L
sodium cyanide	45 g/L

3. Zinc-iron alloy plating bath

zinc ions	18 g/L
iron ions	0.3 g/L
sodium hydroxide	120 g/L
BASE-R	100 g/L (a complexing agent available from

Nippon Hyoumenn Kagaku Corp.)

4. Zinc-nickel alloy plating bath

zinc ions                      10 g/L

nickel ions                    1.8 g/L

sodium hydroxide              120 g/L

NI-T                            100 g/L (a complexing agent available from

Nippon Hyoumenn Kagaku Corp.)

【 0 0 1 7 】

The results of examples 1 to 10 and comparative examples 1 to 12 are shown in Table 1, wherein the source of zinc ions and the zinc dissolution accelerating metal were brought into direct contact.

【 0 0 1 8 】

<Table 1>

【 0 0 1 9 】

The results of examples 11 to 14 and comparative examples 13 to 16 are shown in Table 2, wherein the source of zinc ions and the zinc dissolution accelerating metal were put in different baths and connected via the electric conductor.

【 0 0 2 0 】

<Table 2>

【 0 0 2 1 】

EFFECT OF THE INVENTION

The above examples showed that contacting the source of zinc ions with the zinc dissolution accelerating metal and moving them by rotating, shaking, etc. enables zinc dissolution to accelerate considerably and zinc to dissolve stably, which allows the size of the zinc dissolution bath to decrease and contributes to space saving. Moreover, controlling the degree of contact both or either of the source of zinc ions and the

zinc dissolution accelerating metal have with the plating solution in the dissolution baths according to the analysis of zinc ion concentration in the plating solution enables a stable control of zinc ion concentration and quality zinc plating products to be provided.

[Table 1]

	the source of zinc ions – the zinc dissolution accelerating metal (direct contact)	Barrel rotation	Dissolution rate	
			1st time	5th time
1. Zinc plating zincate bath				
example1	A – (1)	Yes	360 min	360 min
comparative example1	A – (1)	No	(*)	
example2	A – (2)	Yes	300 min	300 min
comparative example2	A – (2)	No	(*)	
example3	A – (3)	Yes	120 min	120 min
comparative example3	A – (3)	No	180 min	240 min
example4	A – (4)	Yes	180 min	180 min
comparative example4	A – (4)	No	240 min	360 min
example5	B – (1)	Yes	120 min	120 min
comparative example5	B – (1)	No	180 min	270 min
example6	C – (1)	Yes	120 min	120 min
comparative example6	C – (1)	No	150 min	210 min
comparative example7	A – (6)	Yes	(*)	
comparative example8	A – (6)	No	(*)	
2. Zinc plating cyanide bath				
example7	A – (2)	Yes	300 min	300 min
comparative example9	A – (2)	No	420 min	450 min
3. Zinc-iron alloy plating bath				
example8	B – (1)	Yes	90 min	90 min
comparative example10	B – (1)	No	120 min	180 min
4. Zinc-nickel alloy plating bath				
example9	A – (5)	Yes	60 min	60 min
comparative example11	A – (5)	No	120 min	150 min
example10	C – (5)	Yes	60 min	60 min
comparative example12	C – (5)	No	90 min	120 min

(\*) = The test was stopped after 480 min of operation because designated increase in zinc ion concentration was not obtained.

[Tabl 2]

	the source of zinc ions – the zinc dissolution accelerating metal (connected via an electric conductor)	Barrel rotation	Dissolution rate	
			1st time	5th time
1. Zinc plating zincate bath				
example11	A – (1)	Yes	450 min	450 min
comparative example13	A – (1)	No	(*)	
example12	A – (2)	Yes	360 min	360 min
comparative example14	A – (2)	No	(*)	
example13	A – (3)	Yes	180 min	180 min
comparative example15	A – (3)	No	300 min	480 min
example14	A – (4)	Yes	210 min	210 min
comparative example16	A – (4)	No	330 min	450 min

(\*) = The test was stopped after 480 min of operation because designated increase in zinc ion concentration was not obtained.